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METHOD OF PRODUCING TITANIUM ALLOYS

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7 Claims. (Cl. 75—135)

1

This invention relates to metallurgical processes and more particularly to a method of producing alloys consisting principally of titanium.

In the manufacture of titanium and the various alloys of titanium wherein the major constituent or base of the alloy consists of titanium, the major problem involved is to prevent the formation of oxygen, nitrogen and hydrogen compounds of titanium which, even in extremely small amounts, embrittle titanium often to the extent of rendering it hot short and usually to the extent of rendering it cold short and substantially unworkable.

In my prior Patent No. 2,205,854 dated June 25, 1940, I have disclosed and claimed a method of producing titanium, substantially free of embrittling oxide, nitride and hydride compounds and cold malleable which method consists in causing a halide compound of titanium, such as the tetra chloride, to chemically react with an alkaline earth metal, such as magnesium, at an elevated temperature below the boiling point of the alkaline earth metal and in an inert atmosphere at a pressure approximating normal or atmospheric pressures. In the practice of this method the titanium tetra chloride in its liquid anhydrous phase substantially free of precipitated titanium oxide compounds, is fed relatively slowly into a molten alkaline earth metal bath, preferably magnesium, heated to temperatures not in excess of the boiling point, while maintaining an inert atmosphere, preferably argon, at atmospheric pressure in a reaction chamber enclosing the bath and contacting tetra chloride. By means of this reaction, titanium metal substantially free of oxide, nitride and hydride compounds is prepared, which on being separated from the contaminating excess magnesium and the magnesium chloride reaction product associated therewith in the manner disclosed in the patent, may be consolidated and sintered into a coherent metal body of high hot and cold ductility.

The object of the present invention is to provide a method of forming alloys consisting principally of titanium by the practice of the general method disclosed in my said patent.

Another object is to provide a method of forming anhydrous metal chlorides.

Still another object is to provide a method of obtaining liquid mixtures consisting mainly of titanium tetra chloride and in minor part of another metal chloride which mixture is substantially free of metal oxides or contained water, for reduction in accordance with the invention of my said patent.

2

A further object is to provide alloys consisting mainly of titanium and in minor part of a metal whose chloride compound is reducible by an alkaline earth metal, particularly magnesium, in accordance with the method of my said patent.

A still further object is to provide a new type getter material for electron and gaseous conduction discharge devices.

Other objects will be apparent as the invention is hereinafter more fully disclosed.

In accordance with the above objects I have discovered that liquid titanium tetrachloride possesses the unique property of dissolving other metal chloride compounds to form therewith, by reaction with any water present in the other metal chloride, anhydrous and oxide-free chloride solutions which are suitable for reduction in accordance with the invention of my above noted patent to form titanium alloys of the dissolved other metal chloride.

The solvent action of titanium tetrachloride for other metal chlorides varies widely, as one skilled in the art would expect, depending upon the particular other metal chloride involved and upon the temperature of the solution. It is extremely difficult to produce anhydrous and oxygen-free metal chlorides for solution in titanium tetra chloride, and most metal chlorides contain either oxygen held in the form of oxide, oxy-chloride or water held as water of crystallization, water of combination or as surface adsorbed water. Titanium tetrachloride, however, is highly reactive with water forming titanium oxide and liberating hydrogen chloride. This reaction is so strong that upon dissolving any metal chloride in titanium tetrachloride all water present in the metal chloride is converted to titanium oxide and is precipitated out of solution together with any oxide or oxide compounds. This precipitated titanium oxide, usually TiO_2, can readily be removed by filtration, decantation or centrifuging from the solution. To effect filtration it is often necessary to heat the solution, sometimes to as high as its boiling point, to obtain a filterable liquid phase. The entire process of dissolving the metal chloride in the titanium tetra chloride, heating and filtering the same, must be performed in an atmosphere substantially free of water vapor. Pure dry air is a suitable atmosphere but other dry gases can also be used.

This unique property of titanium tetrachloride of dissolving other metal chlorides and of freeing the other metal chlorides, in the process of dissolving, of contained water, may be adapted to a plurality of different useful purposes. It pro-

vides a means for obtaining substantially pure oxide-free, anhydrous metal chlorides by dissolving the metal chloride in the titanium tetra chloride, filtering, decanting or centrifuging the solution, and then removing the tetrachloride solvent to recover the dissolved metal chloride therefrom. It also provides a means for obtaining a mixture of metal chlorides consisting principally of titanium tetra chloride and in minor part of at least one other metal chloride for reduction in accordance with the invention of my prior patent to metal form thereby to obtain one of a plurality of possible alloys having titanium as a base.

In the preparation of anhydrous metal chlorides in accordance with the present invention several alternative methods are available. One method involves the use of a sufficient excess of the solvent, titanium tetrachloride, to form at some temperature below the boiling point of the titanium tetrachloride a highly concentrated solution of the metal chloride which, after filtering, decanting or centrifuging, is heated under reduced pressures to temperatures effective to distil off substantially all of the titanium tetrachloride leaving the anhydrous metal chloride behind as a residue. Another method is one wherein the amount of titanium tetrachloride employed is calculated with respect to the solubility of the metal chloride therein at temperatures closely approximating the boiling point of the solvent tetrachloride to produce a saturated solution which, after filtering while hot, is cooled to very low temperatures to effect precipitation of the dissolved metal chloride. After filtering off, decanting or centrifuging, the precipitated metal chloride and subjecting the same to vacuum distillation to remove the residual titanium tetrachloride content thereof, an anhydrous metal chloride product is obtained. Other methods of procedure will be apparent to one skilled in the art.

In the adaptation of this characteristic solvent reaction of titanium tetrachloride to the preparation of a chloride solution suitable for reduction in accordance with the invention of my said patent, the primary object is to dissolve in the titanium tetrachloride such an amount of the chloride compound of the metal desired as a minor alloy constituent in the titanium as will, on reduction with the titanium tetra chloride, provide the desired amount of the metal as an alloy constituent in the titanium. The specific amounts of metal chloride employed may vary widely without essential departure from the present invention, depending upon the metal chloride involved, and the type of alloy involved.

A large number of alloys are possible of production in accordance with the present invention. Practically all metal chlorides have been found to have some solubility in titanium tetra chloride. Also practically all metal chlorides except the alkali metal chlorides are reducible by alkaline earth metals and magnesium in accordance with the invention of my said patent. There is, accordingly, a wide choice of alloy compositions producible in accordance with the present invention.

As a specific embodiment of the invention, but not as a limitation thereof, the preparation of a typical example of an alloy included in the group of alloys consisting principally of titanium and in minor part of at least one of the other so-called rare metals, will be described. This group of alloys offers wide possibilities for adaptation as getter agents in the clean-up of gases

in all types of evacuated and gas-filled electrical devices, such as lamps, radio tubes, gaseous conduction discharge devices, electron discharge devices, etc. In such devices it is customary to employ such a getter agent to clean up residual atmospheric gases, such as oxygen, nitrogen and hydrogen, within the device after sealing the same from the atmosphere. The highly oxidizable so-called "rare metals" have heretofore been found highly suitable for such clean-up purposes due to their low vapor pressure and to their universal property of forming highly stable compounds with oxygen, nitrogen and hydrogen. The major difficulty, heretofore, has been to prepare these metals in a metallic form sufficiently free of these compounds to utilize these properties. By the practice of the present invention titanium alloys of one or more of these metals may be prepared in a high state of purity admirably well suited for use as gas clean-up or getter agents in said devices.

By the term "rare metals" is meant those metals of the zirconium, vanadium and chromium groups, i. e., Zr, Hf, Th, V, Cb, Ta, Cr and U.

The chloride compounds of each of these metals are well known and various methods have heretofore been disclosed in the art for producing the same. The particular method of producing these metal chlorides in their substantially anhydrous oxide-free condition, per se, forms no part of the present invention, except insofar as that method is improved or modified by the practice of the method of the present invention adapted to the forming of oxide-free, anhydrous metal chlorides as hereinabove disclosed.

Of the large number of possible alloys of titanium with one or more of the rare metals, the type of alloy most suitable for use as a gas clean-up or getter agent is the alloy with one or more of the metals of the vanadium group (V, Cb and Ta). An alloy of titanium and one of the metals of the vanadium group inherently possesses high chemical activity towards each of the gases oxygen, nitrogen and hydrogen. In addition to this property, these alloys inherently possess a remarkably high creep strength and resistance to deformation or stiffness even at relatively high temperatures. This property is particularly valuable in connection with the use and adaptation of these alloys as lead-in and support wires in various types of electrical discharge and electronic devices, such as gaseous condensation discharge devices, radio tubes, and the like.

Of the vanadium group metals, I prefer to employ tantalum rather than columbium or vanadium, for the reason that this metal in amounts ranging from 10 to 25% imparts to the oxide-, nitride- and hydride-free titanium relatively high cold workability thereby providing for ready conversion of the alloy into relatively thin strip or small diameter wire which facilities the utilization of the material in the electrical device. Various titanium-tantalum alloys may be formed and all of them are utilizable as getter agents, as even a small percentage of Ta in the Ti markedly increases the hydrogen reactivity of the titanium. The alloy I have found most suitable as a getter agent, however, is one that contains about 20% Ta. This alloy is highly cold ductile and may be easily cold worked down into relatively thin sectioned strip or small diameter wire. The major advantage of such thin sectioned strip or small diameter wire is that such products may be more economically and easily mounted within the radio tube or other such device and the

amount thereof employed may be more easily regulated. Columbium and vanadium alloys of titanium, however, possess good cold working properties.

In the preparation of the preferred titanium-tantalum alloy of the present invention, I follow the general practice outlined above with the following added details:

Tantalum chloride ($TaCl_5$) prepared by any heretofore proposed method which is as near anhydrous and oxide-free as possible to obtain by said prior art method, is dissolved in titanium tetrachloride under a moisture free atmosphere, the solution is filtered, decanted or centrifuged, free of insolubles and oxides, and is reduced precisely as described in my said patent, using molten magnesium as a reducing agent. The reduced metal is recovered and converted to coherent substantially pure form, i. e., free of magnesium and magnesium chloride, by the general procedure outlined in my said patent, and the resultant coherent Ti-Ta alloy, then is cold worked down to thin section strip or small diameter wire, as may be preferred, utilizing equipment and methods well known in the art. The resultant strip or wire product, after surface cleaning, is then cut up into small pieces for use as getter material in the usual manner in the evacuated or gas-filled electrical devices mentioned above. No particular difficulty attends the use and adaptation of this new getter material in the art. It may be welded or mechanically secured in position in the device and being metallic it may be readily heated by induction heating to the reaction temperature which is in the neighborhood of a bright red heat.

In the manufacture of this alloy, I have found that at 25° C., titanium tetrachloride will dissolve about 14 to 15% $TaCl_5$ while at about the boiling point of $TiCl_4$ (136.4° C.) about 40% $TaCl_5$ will dissolve in $TiCl_4$. These figures are based on weight dissolved per unit weight of solvent.

The solubility of $CbCl_5$ in $TiCl_4$ is much lower being in the neighborhood of .24% at 25° C. and 2% at 136.4° C. Zirconium chloride, on the other hand, has a greater solubility in $TiCl_4$, being in the neighborhood of 30% $ZrCl_4$ at about 25° C.

I prefer to employ, in the forming of about a 20% Ta alloy of titanium, a solution that contains in the neighborhood of 11.5 grams $TaCl_5$ per hundred. This solution is freely liquid at atmospheric temperatures and is readily filterable free of insoluble materials present therein, and upon reduction by molten magnesium, in accordance with the method of my said patent, yields consistently about a 20% Ta alloy.

In the reduction of anhydrous solutions of one or more of the rare metal chlorides in titanium tetra chloride by magnesium in accordance with the method of my said prior patent, the relative proportions of the titanium chloride and the rare metal chlorides dissolved therein are adjusted to approximate that providing on reduction the approximate desired percentage of the associated metal in the titanium metal. In some instances this requires the incorporation in the titanium tetrachloride of a larger amount of the dissolving metal chloride than normally may be held in solution at any temperature below the boiling point of the titanium tetrachloride, and may require the use of a suspension or slurry consisting of titanium tetrachloride saturated at the temperature of heating with metal chloride and containing suspended undissolved anhydrous metal chloride. Some suspensions or slurries, for example, are readily produced by dissolving the desired amount of metal chloride in a sufficient volume of titanium tetrachloride to effect complete solution of the same, filtering the solution to remove titanium dioxide formed as a result of reaction of the titanium tetrachloride with water present in the metal chloride, and then evaporating off the excess titanium tetrachloride in any convenient manner, as by vacuum distillation.

By the use of solutions of various metal chlorides in titanium tetrachloride reduced to metallic form by magnesium in accordance with the invention of my above noted patent, I have been able to produce a large number of different titanium base alloys which, being substantially free of the embrittling constituents oxygen, nitrogen, carbon and silicon, are usually ductile and workable either when hot or when cold. The physical, chemical and metallurgical properties of these alloys have not as yet been fully determined. Many of these alloys appear promising as corrosion resistant alloys; others appear promising for special fields of use, such as electrode and getter materials in electronic devices; still others offer considerable possibilities for adaptation as electrical contact elements in various types of electrical devices.

It is believed apparent to any one skilled in the art that any metal chloride may be substituted for $TaCl_5$ in the above specific example without essential departure from the present invention; and that various mixtures of rare metal chlorides may alternatively be employed to produce various complex alloys consisting mainly of titanium and in minor part of one or a plurality of associated rare metal alloy constituents. Various other highly reactive metals utilizable as getter materials may be substituted for Ta, in part or in whole, in the specific example given above without essential departure therefrom, such as one or more of the rare earth metals, vanadium, columbium, zirconium, hafnium, thorium, uranium, etc.

The essential step involved in the forming of any solution of metal chlorides in titanium tetrachloride is to separate the solution free of precipitated titanium oxide (TiO_2) prior to reducing the solution in accordance with the invention of my said co-pending application. Titanium tetrachloride, being a liquid at atmospheric temperatures and not boiling at temperatures below about 136.4° C., presents no great difficulties as a solvent for other metal chlorides except that during the production of the solution, the filtering of the same, and the introduction of the solution into the reducing furnace, the solution should be protected against reaction with water vapor.

As hereinabove indicated, in place of a rare metal, substantially any other metal chloride except the alkali metal chlorides may be substituted in part or in whole for tantalum in the above specific embodiment of the present invention without departure from the present invention, to obtain thereby titanium-base alloys containing from one to a plurality of associated metals as minor alloy constituents. It is not possible to describe all of these alloys or to describe the various physical and chemical properties of the alloys. The method of preparing these alloys hereinabove described, however, may be universally applied in the forming of all such titanium-base alloys, as one skilled in the art will recognize.

Having hereinabove disclosed the present invention generically and specifically and given

several specific examples of the same, it is believed apparent that the invention is adapted for wide modification without essential departure therefrom and all such modifications and adaptations are contemplated as may fall within the scope of the following claims.

What I claim is:

1. The method of forming a completely dehydrated metal chloride which comprises dissolving a substantially dehydrated metal chloride in liquid titanium tetrachloride, separating the liquid and solid phases obtained thereby, and separating the titanium tetrachloride of the liquid phase from the metal chloride contained therein.

2. The method of forming a completely dehydrated metal chloride which comprises dissolving a substantially dehydrated metal chloride in liquid titanium tetrachloride, separating the liquid phase chlorides from the solid phase materials present therein, and distilling off the titanium tetrachloride content of the liquid phase to recover the metal chloride content dissolved therein.

3. The method of forming anhydrous tantalum chloride which comprises dissolving substantially dehydrated tantalum chloride in liquid titanium tetrachloride, separating the liquid phase chlorides from the solid phase materials present therein, and heating the liquid phase chlorides to a temperature effective to vaporize the titanium tetrachloride only.

4. The method of forming anhydrous metal chlorides which comprises suspending a substantially anhydrous metal chloride in liquid titanium tetrachloride, heating the suspension to a temperature not in excess of the boiling point of the titanium tetrachloride to obtain a saturated solution of the suspended chloride therein, filtering the solution while hot to separate the solution from the insoluble materials contained therein, cooling the solution to precipitate therefrom the said other metal chloride in excess of the solubility limit at said lower temperature, and separating the liquid and solid phase chlorides resulting.

5. The method of producing titanium-base alloys substantially free of embrittling oxide, nitride and hydride compounds which comprises forming a liquid phase mixture of metal chlorides consisting predominantly of titanium tetrachloride and in minor part of at least one other metal chloride which is soluble in the liquid phase titanium tetrachloride, filtering the same to remove oxygen-containing insolubles therefrom and reducing the filtered mixture to metal powder form by reacting the same with molten magnesium under an inert gas maintained at atmospheric pressure, separating the metal powders obtained from the excess magnesium and from the magnesium chloride product of the reduction reaction, and compacting and sintering the recovered metal powders to coherent metal in an inert atmosphere.

6. The method of claim 5, wherein said other metal consists of a metal of the rare metal group.

7. The method of claim 5, wherein said other metal consists of tantalum.

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